

# PATENT SPECIFICATION

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## (54) LIQUID COATING COMPOSITION WITH A LOW-SOLVENT OR SOLVENT-FREE BASE

(71) We, CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT, a German Company, of 4370 Marl, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to liquid coating compositions with a low-solvent or solvent-free base, wherein the coating compositions—which may contain other conventional ingredients—contain as binder a mixture of aminoplast resins and polyesters.

This kind of environmentally suitable coating composition has been known for some years now (U.K. Patent Specification No. 1,345,907). Equally well known are coating compositions which contain polyesters with acid components which are formed entirely or partly of hexahydroterephthalic acid units (U.K. Patent Specifications 1,242,005, 1,471,779, U.K. Patent Application 43296/75 (Serial No. 1,515,558) and German laid-open application DOS 2,437,217). U.K. Specification 1,242,005 does not claim expressly a low solvent or solvent-free coating medium. U.K. Specification 1,471,779 mentions only aromatic dicarboxylic acids with carboxyl groups in 1.2 orientation or 1.3 orientation as the acids which can be used besides hexahydroterephthalic acids. U.K. Patent Application No. 43296/75 (Serial No. 1,515,558) is directed towards the same end and requires hexahydroterephthalic acid to constitute at least 80 mol per cent of the acid component of the polyester but allows the remainder to consist of other polyester-forming aromatic and (cyclo)-aliphatic carboxylic acids.

As exhaustive special tests have shown, the coating compositions known in the art have a crucial disadvantage: if coatings which fulfil the normal high requirements are to be obtained, then up to the present time stoving temperatures of  $>130^{\circ}\text{C}$ , and generally also of  $>150^{\circ}\text{C}$  have to be used (DOS 2 437 217, Example 3). In order to cut energy costs, stoving temperatures should be reduced—naturally, while still retaining the good final characteristics. Although it is possible with the prior art products to use stoving temperatures of  $<150^{\circ}\text{C}$  or  $<130^{\circ}\text{C}$ , it is necessary then to extend the stoving time considerably, so that hardening is no longer economical or practical. Neither do larger quantities of catalysts produce the desired result, since these can impair the characteristics of the coating, such as its gloss, for example.

DOS 2 437 217 describes coating media which, according to the examples, can be stoved at  $120^{\circ}\text{C}$  in an acceptable time, and which give good coatings. However, actual tests have shown that, unlike the other products in the state of the art cited previously above, the coating media described in this instance cannot be stoved at temperatures of  $170$  to  $180^{\circ}\text{C}$ , which is the temperature required in practice for certain production processes, without flaws occurring in the coating. These flaws which occur at higher temperatures make the binders according to DOS 2 437 217 extremely critical with increased thermal loading such as can arise, for example, when a belt is held stationary during series lacquering. In addition, during the stoving process these coating media do not display adequate stability such as is shown by the coating media described in U.K. patent application No. 43296/75 (Serial No. 1,515,558).

The present invention seeks to develop a coating medium which can be stoved

at stoving temperatures below 130°C, while retaining the good characteristics which are already known for this group of products.

According to the present invention there is provided a low-solvent or solvent-free liquid coating composition containing as binder

- 5 A) 45 to 10 percent by weight of an aminoplast resin and/or low molecular weight precursor(s) thereof .5
- and
- 10 B) 55 to 90 percent by weight of an at least bifunctional polyester or polyester mixture bearing predominantly free hydroxyl end groups optionally together with carboxyl end groups, 10
- the polyester(s) of Component B) being produced by condensing a component I, consisting of
- 15 I.1. 0 to 50 mole percent of one or more aliphatic polyols with 3 to 4 hydroxyl groups and 3 to 6 carbon atoms 15
- and
- 15 I.2. 100 to 50 mole percent of a mixture II of aliphatic and cycloaliphatic diols, the mixture II in turn consisting of
- 20 II.1. 10 to 90 mole percent of ethylene glycol
- and
- 20 II.2. 90 to 0 mole percent of propane diol-(1,2) 20
- and
- 25 II.3. 0 to 40 mole percent of one or more other aliphatic or cycloaliphatic diols in which the hydroxyl functions are separated by 2 to 8 carbon atoms and up to 2 of the carbon atoms can be replaced by oxygen atoms which in turn are separated from each other and from the hydroxyl groups by at least 2 carbon atoms, 25
- with a component III, consisting of a mixture of
- 30 III.1. 67 to 92 mole percent hexahydroterephthalic acid and 30
- III.2. one or more aromatic dicarboxylic acids, optionally followed by acidification, e.g. with trimellitic acid anhydride, to increase the acid number, the polyester or polyester mixture used as Component B) having a molecular weight of 300 to 1,500 and the binder being optionally obtained by combined condensation of the aminoplast resin and/or low molecular weight precursor(s) thereof with the polyester(s) or by combined condensation of the basic material used to produce the aminoplast resin with the polyester(s), in which process terephthalic acid is used as Component III.2 in an amount of from 8 to 33 mole percent based on component III. 35
- 40 Preferably component III.2, i.e. terephthalic acid, is present in an amount of from 12 to 25 mole percent based on component II. 40
- For the polyols according to Component I.1, glycerol, trimethylolethane, tri methylolpropane and pentaerythritol can be used, for example; the use of glycerol and trimethylolpropane is recommended.
- 45 Component I.1 is preferably contained in the polyesters according to B. in amounts of from 0 to 20 mole percent; accordingly, the polyesters preferably contain mixture II (=Component I.2) in amounts of from 80 to 100 mole percent. 45
- 50 For the diols of Component II.3, propane diol-(1,3), butane diol-(1,2), butane diol-(2,3), butane diol-(1,3), butane diol-(1,4), 2,2-dimethylpropane diol-(1,3), hexane diol-(1,6), 1,4-di-(hydroxymethyl)-cyclohexane, x.8-di-(hydroxymethyl)-tri-cyclo-[5.2.1.0<sup>2,6</sup>]decane where x stands for 3, 4 or 5, diethylene glycol or dipropylene glycol can be used, for example. Cycloaliphatic diols can be used in their cis- or trans-form or as a mixture of both forms. 50
- 55 Component II.3 is preferably added in amounts of from 0 to 30 mole percent, and preferably both Component II.1 and Component II.2 are present. When propane-diol-(1,2) is present it suitably constitutes 10 to 90 mol per cent of mixture II. 55
- 60 The hexahydroterephthalic acid is preferably contained in the acid component (Component III) in amounts from 75 to 88 mole percent. The acids can be used as free acids for the preparation of the polyesters. However, it is recommended that the lower alkyl esters be used in the reaction, dimethylesters being particularly recommended. For the dimethylhexahydroterephthalate, a cis- or trans- isomer is recommended, such as is obtained when dimethylterephthalate is high-pressure hydrogenated. 60
- Preferably, the polyesters used according to the invention have a molecular weight

of from 600 to 1,000. Molecular weight is taken as the mean molecular weight which is determined by end group titration. The additional inclusion of polyols with more than 2 hydroxyl groups increases the viscosity of the polyesters according to the invention. The viscosity can also be controlled, if required, by the additional use of diols (II.3). The inclusion of longer chain linear diols reduces the viscosity, whereas branched or cycloaliphatic diols bring about an increase in viscosity.

The relationship of Components III.1:III.2 is critical for the polyesters used according to the invention. With a lower content of terephthalic acid or the lower alkyl esters thereof than is specified according to the invention, at stoving temperatures of 120°C, for example, only insufficiently hard coatings will be obtained, whereas if the terephthalic acid content is too high then crystalline products which cannot be dissolved in normal lacquer solvents will result.

The preparation of the esters can be carried out according to any known and normally used method—with or without a catalyst, with or without a stream of inert gas—by solvent condensation, melt condensation or azeotropic esterification at temperatures up to 250°C, or at even higher temperatures if required; the water or methanol, for example, which is liberated during the process is removed. Esterification can be controlled by determination of the hydroxyl-value and, if the free dicarboxylic acid are employed, additionally by determination of the acid value. Generally, the esterification conditions are selected so that the reaction is as complete as possible. The molecular weight of the ester can thus be controlled by the ratio of the added alcohol component (diol or polyol, as applicable) and the added dicarboxylic acid or its ester.

If part of the acid component is added in the form of the free acid and the rest as an alkyl ester, it is advisable to carry out the reaction in two consecutive stages. In the first stage the alkyl ester will be transesterified with some or all of the diols and/or polyols until the alcohol is almost completely eliminated. After this, the remaining components are added and condensed with distillation of the water until the desired degree of reaction has been obtained.

If more highly reactive aminoplast resins which harden without the addition of strongly acid catalysts are used, it is advantageous to add polyesters with acid number of up to 30 mg KOH/g, and preferably up to 20 mg KOH/g. This kind of product can be obtained when the free dicarboxylic acids are used by interrupting the reaction at the desired acid value, for example. The acid value of polyesters of this kind, obtained by transesterification, which have virtually no free carboxyl end groups, or polyesters produced by esterification with an acid number of <5 mg KOH/g, can be further greatly increased by reaction at 130 to 190°C with relatively strongly acid carboxylic acids or anhydrides thereof such as maleic acid, phthalic acid, trimellitic acid or pyromellitic acid, for example, the two last named being the most preferred of these. Preferably, these types of polyester are acidified until they have an acid number in the region of >5 to 20 mg KOH/g.

The esterification or transesterification temperature is selected so that the losses of very volatile substances which make up the esters according to the invention remain small, i.e. at least the first period of esterification is carried out at a temperature which lies below the boiling point of the basic substance with the lowest boiling point.

The properties of the coatings produced from the polyesters used according to the invention depend on the average molecular weight, the functionality and the composition of the polyester. With higher average molecular weight, the hardness of the lacquer film is generally reduced, while the elasticity increases. Conversely, with lower molecular weights the flexibility of the lacquer film is reduced, with a simultaneous increase in the hardness.

The differences in the composition of the polyester also have a similar kind of effect. With an increased amount of hexahydroterephthalic acid units in the polyester chain, the elasticity of the lacquer film is increased, while its hardness is reduced. With increasing chain length of the open-chain diols (II.3) which are used additionally in subordinate amounts, and with an increasingly large proportion of these diols in the polyester, the lacquer film becomes softer and more flexible. However, if diols with short and branched carbon chains or with cycloaliphatic rings are used additionally in the preparation of the polyesters, then the coatings produced from these esters generally give harder and less elastic films as the proportion of these diols is increased.

The molar ratio of polyol to diol is significant for the mechanical properties of the lacquer film: with a reduced molar ratio of polyol to diol the hardness of the film is also reduced, while its elasticity is increased. Conversely, with a greater molar ratio

of polyol to diol, the flexibility of the lacquer film is reduced and its hardness is improved.

Knowledge of these laws makes it possible for a worker in the field to select without difficulty, within the scope of the range claimed, the polyesters with the optimum properties for the purpose for which the coating medium according to the invention is to be used.

The known reaction products of aldehydes, and particularly formaldehyde, with several amino group or amido group bearing substances, including, for example, melamine, urea, dicyandiamide and benzoguanamine, can be considered suitable aminoplast resins. Mixtures of these types of substance are also suitable. Aminoplast resins modified with alcohols are particularly suitable.

Preferably, due to their low substantial viscosity, lower molecular, structurally-defined aminoplast resins which can be mixed virtually indefinitely with the polyesters used according to the invention will be used. Structurally-defined aminoplast resins of this kind include dimethylolurea, tetramethylolbenzoguanamine, trimethylolmelamine or hexamethylolmelamine, for example. The latter can also be used in partially or completely etherified form, such as dimethoxymethylurea, tetrakis-(methoxymethyl)-benzoguanamine, tetrakis-(ethoxymethyl)-benzoguanamine, products of the partial or complete etherification of hexamethylolamine, such as tetrakis-(methoxymethyl)-dimethylolmelamine, pentakis-(methoxymethyl)-monomethylolmelamine and hexakis-(methoxymethyl)melamine, as well as mixtures of these three substances or hexakis-(butoxymethyl)-melamine. Hexamethylolmelamine derivatives etherified with alcohols with 1 to 4 carbon atoms, which are fluid in substance at room temperature, are particularly recommended.

When these aminoplast resins are used, the addition of strongly acid catalysts such as p-toluene sulphonic acid is recommended to accelerate hardening. In order to obtain lacquers with good storing stability the use of blocked catalysts is particularly recommended.

In one preferred embodiment more highly reactive, higher molecular melamine resins with relatively low viscosity, specially developed for low solvent content stoving lacquers are used; with the polyesters which bear a subordinate amount of carboxylic end groups, these harden to hard elastic films without the addition of a catalyst. These melamine resins, which are generally partially etherified with methanol and which still have a considerable proportion of un-etherified methylol groups, are described, for example, by L. A. Rutter (*Adhesion 1974*, (Vol. 6), page 178; group II amino-resins).

Naturally, the polyesters which are to be used according to the invention can also be combined with higher molecular aminoplast resins. Generally, the polyesters according to the invention can be mixed with these types of aminoplast resins in the mixture proportions claimed without the occurrence of cloudiness. However, should the mixing of resinous aminoplasts with the polyesters according to the invention result in cloudiness, compatibility can be improved if the polyesters and the aminoplast resins are allowed to react in a known way in substance form or in solution; care must be taken to ensure that the reaction does not continue until crosslinking occurs. This can be accomplished, for example, by heating the mixture or solutions of the two resins for a short time, appropriately in the presence of a catalyst such as organic or mineral acids, for example.

It is also possible to add the polyesters used according to the invention to the basic substances before or during the preparation of the aminoplast resins from, for example, urea, benzoguanamine or melamine and aldehydes; naturally, it is also possible to use as well additional normal alkanols to modify the aminoplast resin thus formed. The methods for producing these kinds of amino-aldehyde resins are known. There are a number of commercial aminoplast resins available for combination with the polyesters used according to the invention.

To produce the coating compositions, generally the ester and the aminoplast resin or aminoplast resin solution are mixed together first. The weight ratio of polyester to aminoplast resin can vary between 55:45 and 90:10, preferably it will lie between 65:35 and 85:15. The ratio for the two components which is best for the actual purpose for which the lacquer is to be used can easily be determined by preliminary tests. It should be borne in mind here that normally, by increasing the aminoplast resin portion, the hardness of the coating is increased and the elasticity reduced, while a reduction of the aminoplast resin portion reduces hardness and increases flexibility.

According to the application desired for the coating composition, its viscosity can be reduced by the addition of small amounts of normal polar lacquer solvents such as

propanol, i-propanol, butanol, ethylacetate, butylacetate, ethyl glycol, ethyl glycol acetate, butylglycol, methylethylketone, methylisobutylketone, cyclohexanone, 2-nitropropane, trichloroethylene or mixtures of various solvents of this kind. It is also possible, and may be worth recommending for economic reasons, to add greater or lesser amounts of less polar solvents, such as xylene, aromatic compounds with higher boiling points or aliphatic hydrocarbon mixtures, such as mineral spirits, for example. The proportional quantity of these less polar solvents which is added can be chosen freely within the limits of the solubility of the polyesters used according to the invention, and their compatibility with the aminoplastic resins used. According to the invention, in no instance is more than 30 percent by weight of solvent used in the coating composition, and it will be understood that compositions containing up to 30 weight percent solvent are low-solvent compositions, in the context of this invention.

In addition to greater amounts of pigment, the coating compositions according to the invention can contain the normal additives and supplementary substances, particularly flow agents and other additional binders, such as epoxy resins and silicone resins which contain hydroxyl groups, for example.

The binder:pigment weight ratio is determined by the purpose for which the relevant coating is to be used. Thus, the binders are pigmented in the weight ratio of 1:0.3 to 1:1 when they are used for the production of external car lacquers or for industrial lacquers. Even with a binder:pigment ratio of 1:1.1 to 1:1.3 as is normal for packaging lacquers or for coil-coating, the coatings display unusually good properties. The coating compositions according to the invention can also have a still higher pigment content, such as is normal for the production of primers.

The coating compositions may be applied by normal methods, such as with a brush, by spraying, dipping or rolling—cold, warm or hot—and is stoved at temperatures between 100 and 250°C, preferably between 110 and 200°C and particularly between 120 and 180°C. When almost completely etherified hexamethylolmelamine derivatives are used, an acid catalyst such as p-toluene sulphonic acid, for example, is added to accelerate the hardening process. Since the use of such strongly acid catalysts can increase the viscosity of the coating compositions even at room temperature, it is advisable to use blocked catalysts which do not produce their catalytic effect until higher temperatures are reached. For reasons of improved storing stability and better electrostatic workability, the use of blocked acids such as those described in DT—AS 2 345 114 or DT—PS 2 356 768 is recommended. When more highly reactive aminoplast resins are used, hardening will preferably be carried out without the addition of catalysts.

The coatings produced according to the invention have an abundance of good properties. They have a high gloss, can be pigmented well and adhere extremely well, particularly to metals. During salt-spray tests, tropical tests and tests in the weatherometer they display outstanding anti-corrosion qualities and weather resistance. Furthermore, they display good storing stability, particularly when non-ionic blocked catalysts or more highly reactive melamine resins without catalysts are used. In addition, the systems are distinguished by good antisag properties on vertical surfaces during the stoving process.

An outstanding feature of the coating compositions according to the invention is the possibility of obtaining hardy elastic coatings even when the stoving temperature is varied over a wide range. The polyester/aminoplast resin binders containing little or no solvent which have been known up to the present time only give tough elastic coatings which are resistant to over-stoving if they are stoved at temperatures of >130°C to >150°C. Although lower stoving temperatures can also be used with the products in the state of the art, with these an extension of the stoving time to a duration which is virtually unacceptable must be taken into account, or else the amounts of catalysts must be increased so much that the quality of the coating is no longer suitable for the practical requirements of all the fields of application. With the coatings according to the invention the disadvantages mentioned can be eliminated. In other words, the coating compositions according to the invention provide the manufacturer with a system with which he can carry out the hardening process irrespective of the kind of stoving unit he has available, both at higher and at lower temperatures.

Since the coating compositions according to the invention contain only a little or no organic solvent, they are exceptionally suitable environmentally, so that the cost of after-burning can be reduced or even eliminated. This fact, together with their good over-stoving stability, make the coating compositions according to the invention particularly suitable for industrial mass-production lacquering.

## Examples.

*I. Preparation of Polyester*

A mixture of 248 g ethylene glycol (4 mol), 76 g propane diol-(1,2) (1 mol), 600 g dimethylhexahydroterephthalate (3 mol) and 194 g dimethylterephthalate (1 mol) is heated for 2 to 3 hours to 180 to 190°C, after the addition of 0.8 ml of a titanium tetraisopropylate solution (10 percent by volume in isopropanol), with agitation, in a gentle stream of nitrogen, and with the methanol formed being continuously removed by distillation. The temperature is thereafter slowly increased to 210°C. After a total of 22 hours, almost 256 g (8 mol) of methanol has been removed. This corresponds to essentially complete (>99%) transesterification of the terephthalates. The clear, colourless ester mixture has an acid number of 0.9 mg KOH/g and a hydroxyl number of 128 mg KOH/g—corresponding to a mean molar weight of 869. An 80 ml % solution of the polyester in ethyl glycol acetate is prepared.

*II. Acidifying of Polyester*

1.72 g trimellitic acid anhydride is added to 100 g of a solvent-free polyester according to I, at 170°C, with agitation, and is left at this temperature, under nitrogen, for around 1 hour. The product obtained has an acid number of 9.7 mg KOH/g after cooling. The polyester is then dissolved in ethyl glycol acetate to form an 80 ml % solution.

*III. Preparation of Binder*

The polyester or the polyester solution is mixed with a commercial hexamethylol-melamine derivative or a solution of a melamine formaldehyde alkanol condensate with the desired ratio of solid matter. If the ester and the aminoplast resin are not compatible with each other, then the mixture of the two components, which contains solvent when aminoplast resin solutions are used, is heated for 10 to 60 minutes to 50 to 100°C.

*V. Preparation and Testing of Coating*

To prepare a coating composition, pigmentation is carried out—if appropriate, after the addition of solvents—in the desired binder:pigment ratio, by working in the appropriate amount of pigment, for example, on a three-roller mill.

*V. Testing Preparation and Testing of Coating*

To test the coating composition, this is applied to sample metal and glass plates at room temperature, and stoved. To reduce the stoving temperature when less reactive aminoplast resins are used, p-toluene sulphonic acid or a non-ionic blocked catalyst is added. The coating thickness of the film on which the test is carried out generally amounts to around 40 μ. The hardness test is carried out according to DIN 53 157, by determination of the pendulum hardness according to König. The elasticity of the coatings is determined by the Erichsen depression test (DIN 53 156). As a gauge of the ductility, the depression of the lacquered metal sheet at which the coating begins to crack is given in mm. For this testing method, slow deformation of the coating is important (advance: 0.2 mm/sec).

The examples designated by letters of the alphabet are comparative examples. All the details regarding relative amounts, time, etc., which are not given in III to V, can be found in the Tables.

*Example A:*

(U.K. Specification No. 1,471,779, Example 8)

A mixture of 62 g ethylene glycol (1 mol) and 100 g dimethylhexahydroterephthalate (0.5 mol) is heated for 2 to 3 hours up to 180 to 190°C, after the addition of 1 ml of a 10 percent by volume solution of titanium tetraisopropylate, with agitation, in a gentle stream of nitrogen and with continuous removal by distillation of the methanol. The temperature is then slowly increased to 200°C. After a total of 16 hours, about 32 g of methane has been split-off. After cooling the mixture 124 g ethylene glycol (2 mol), 148 g phthalic acid anhydride (1 mol) and 73 g adipic acid (0.5 mol) are added and it is heated according to the following temperature-time plan: 2 hours at 140°C, 2 hours at 160°C, 4 hours at 180°C, 4 hours at 190°C and 3 to 4 hours at 200°C. After extracting around 36 g water, a clear polyester with a hydroxyl number of 237 mg KOH/g and an acid number of 4.7 mg KOH/g, which corresponds to an average molecular weight of around 465, is obtained. From this polyester and a commercial, substantially methyl-etherified hexamethylolmelamine which is fluid in substance at room temperature, together with titanium dioxide, a

coating composition is produced which contains 70 parts polyester, 30 parts aminoplast resin, 80 parts titanium dioxide, 8 parts of a 50 percent solution of a commercial non-ionic blocked acid catalyst and 20 percent by weight ethyl glycol acetate. The coatings which are stoved at 120°/30 min display the following values:

5 (Hardness) H : < 50 sec 5  
(Depression) D : > 10 mm

#### Example B:

(U.K. Application 43296/75—Serial No. 1,151,558, Example 8)

- 10 i. By the method described under Preparation of Polyester, from 3.5 moles of ethylene glycol, 0.5 moles propane diol-(1,2) and 3 moles DMHT a polyester 10  
is prepared with a hydroxyl number of 170 mg KOH/g, corresponding to an average molecular weight of 659. A coating agent is produced from 75 parts of the polyester, 25 parts of the aminoplast resin used in Example A, 80 parts of titanium dioxide, 2.5 or 5.0 parts of a 20 percent isopropanolic p-toluene sul-  
15 phonic acid solution and 43 g ethyl glycol acetate; coatings with the following values are obtained from this: 15

TABLE 1

Stoving Conditions (°C/min)	Type and Amount of Catalyst (% by weight relative to binder)	H (sec)	D (mm)
120/30	0.5 pTS	83	10
120/30	1.0 pTS	127	9.7
120/90	0.5 pTS	149	9.7

- 20 ii. If the 2.5 parts of p-toluene sulphonic acid solution are replaced by 8 parts of the catalyst solution described in Example A, the following coating characteristics result, with 120°/30 min: 20

H : > 50 sec  
D : > 10 mm

- 25 iii. 33.3 g of a commercial solution of a partially methylated, more highly reactive melamine resin (90 percent in isopropanol) is added to 87.5 g of an 80 percent solution in ethyl glycol acetate of the polyester according to Example B.i acidified with trimellitic acid to an acid number of 9.9 mg KOH/g. Pigmentation is then carried out with 80 g titanium dioxide, and after the addition of 24.2 g of ethyl glycol acetate, stoving is carried out at 120°/30 min: 25

30 H : 56 sec  
D : > 10 mm 30

#### Example C:

(DOS 2 437 217, Example 1)

- 35 i. 519.4 g phthalic acid anhydride, 57 g adipic acid, 160 g propane diol-(1,2), 159.6 g ethylene glycol and 81 g neopentyl glycol are heated up over 8 hours while the temperature is gradually increased to 200°C, and react in a stream of nitrogen, with continuous extraction of the reaction water created, until an acid number of 12.6 mg KOH/g is reached; they are then dissolved in ethyl glycol acetate (80 percent). The polyester solution is mixed with hexakis-(methoxy)-methylmelamine to give a solid matter ratio of 80:20, and is then ground with 80 parts titanium dioxide. After the addition of 1 g of a 20 percent isopropanolic p-toluene sulphonic acid solution this is thinned with 24 g ethyl glycol acetate 40

and, after application, is stoved for 30 min at 170°C. The resulting coating is hard and brittle.

H : 188 sec

D : 1.2 mm

- 5 ii. The 80 percent solution of the polyester in Example C/i is mixed with the partially methylated melamine resin described in Example B/iii to give a solid matter ratio of 7:3, and is then pigmented with titanium dioxide in the ratio of 1:0.8. 5

TABLE 2

Stoving Conditions (°C/min)	H (sec)	D (mm)
120/30	126	9.5
170/30	182	0.7

- 10 iii. A coating composition is prepared from 100 parts of the 80 percent polyester solution according to Example C/i, 20 parts of the melamine resin described in Example A, 80 parts of titanium dioxide and 1 part of a 20 percent by weight isopropanolic p-toluene sulphonic acid solution. This is thinned by the addition of ethyl glycol acetate to a viscosity of 40 sec in the DIN 4 mm beaker (20°C). 10
- 15 Next, a 1 mm thick metal plate (70×200 mm) is coated with a doctor blade, so that after stoving in the horizontal position coating thicknesses of  $50 \pm 3 \mu$  would result. The lower part of the plate (5 cm) is not coated. After 10 min airing time the plate is suspended vertically and stoved. (With insufficient antisag properties, a coating thickness gradient develops—the measuring points are 1.5 cm from the upper and lower edges of the coating respectively. With a stronger tendency to flow, runs can be seen in the uncoated lower area of the plate.) 15
- 20 20

TABLE 3

Coating Agent	Stoving Conditions (°C/min)	H(sec)	D (mm)	Coating Thickness ( $\mu$ m) 1.5 cm from Upper Lower Edge		Runs
Example C/iii	120/30	141	10	41	59	Many
	170/30	197	1.6	43	61	Indicated
Example 5a *)	120/30	147	10	48	53	None
	170/30	182	7.8	49	50	None

\*) converted to an acid number of 9.3 with TMAA.

#### Example D.

- 25 A polyester with a hydroxyl number of 163 mg KOH/g and an acid number of 0.6 mg KOH/g, corresponding to a molecular weight of 685, is prepared from 3 mol ethylene glycol, 1 mol propane diol-(1,2), 1.8 mol dimethylhexahydroterephthalate and 1.2 mol dimethylterephthalate by the method described. The product obtained is partially crystalline at room temperature and does not dissolve to become clear in lacquer solvents such as xylene, butyl acetate, n-butanol, ethyl glycol acetate, etc. 25

#### Examples 1—9.

- 30 Data concerning the compositions are set out in Table 4. 30

- 35 All data concerning quantities relate to weight, unless otherwise stated. In each case the polyester is obtained in a manner analogous to 1 above, moer than 99% of the methyl groups of the initial esters being exchanged in the transesterification. The solvent content in Example 1 is 10 wt % and in Examples 2—9 is 20 wt %. The molecular weights of the acidified polyesters in Examples 3, 5b, 6 and 7 are respectively 737, 981, 1038 and 1211, acidification being carried out in a manner analogous to II above. 35



The binder and coating composition are then prepared in a manner analogous to III and IV above and the coating prepared and tested in a manner analogous to V above.

TABLE 4

Example No.	PES prepared by condensation of [Mole]	Mean Molar Weight of PES	Weight Ratio of PES:Aminoplast Resin: TiO <sub>2</sub>	Type of Aminoplast Resin	Type and Amount of Catalyst (% by weight rel. to binder)	Stoving Conditions [°C/min]	H [sec]	D [mm]
1	1.25 EG 1.25 PG 1.275 DHHT 0.225 DMT	385	7.5:2.5:8 "	HMM "	0.5 pTS "	120/30 170/30	173 184	8.9 4.8
2	3 EG 1 PG 2.5 DMHT 0.5 DMT	710	7.5:2.5:0 " 7.5:2.5:8 " 7.5:2.5:0 "	HMM " " " "	0.5 pTS " " 8 Bl. cat. "	120/30 140/30 120/30 140/30 120/30 140/30	224 225 154 162 195 209	>10 >10 9.8 8.2 >10 >10
3	3.2 EG 0.8 CHMD 2.65 DMHT 0.35 DMT (converted to AN9.3 with TMAA)	725	7:3:8 "	MFC "	— —	120/30 160/30	121 171	>10 7.1
4	4 EG 1 PG 3 DMHT 1 DMT	865	8:2:0 " 8:2:8 "	HMM " " "	0.5 pTS " " "	120/30 170/30 120/30 140/30	197 232 157 187	>10 9.8 >10 >10
5a	4 EG 1 CHMD 3.5 DMHT 0.5 DMT	965	7.5:2.5:8	HMM "	0.5 pTS "	120/30 170/30	153 192	9.9 8.7
5b	(converted to AN9.3 with TMAA)		7:3:8	MFC "	— —	120/30 160/30	153 189	>10 8.8

TABLE 4 cont.

Example No.	PES prepared by condensation of [Mole]	Mean Molar Weight of PES	Weight Ratio of PES:Aminoplast Resin: TiO <sub>2</sub>	Type of Aminoplast Resin	Type and Amount of Catalyst (% by weight rel. to binder)	Stoving Conditions [°C/min]	H [sec]	D [mm]
6	1 EG	1020	7 : 2.7 : 8	MFC	—	120/30	139	9.4
	3 PG			"		160/30	170	7.3
	1 CHMD							
	3.5 DMHT							
7	0.5 DMT	1190	7 : 2.7 : 8	MFC	—	120/30	185	9.8
	(converted to AN9.6 with TMAA)			"		140/30	198	8.9
	2 CHMD							
	3.5 DMHT							
8	0.5 DMT	1425	7.5 : 2.5 : 8	HMM	0.5 pTS	120/30	156	>10
	(converted to AN9.6 with TMAA)			"		170/30	189	8.6
	3.5 EG							
	3.5 PG							
9	5.05 DMHT	715	7.5 : 2.5 : 8	HMM	0.5 pTS	120/20	139	9.7
	0.95 SMT			"		120/30	153	9.1
	3.2 EG							
	0.5 PG							
	0.3 Gly		"					
	2.5 DMHT							
	0.5 DMT							

Abbreviations in Table 4

PES Saturated polyester = component B in compositions according to the invention

EG Ethylene Glycol

PG Propane diol-(1,2)

## Abbreviations in Table 4 (cont.)

CHMD 1,4-di-(hydroxymethyl)-cyclohexane  
Gly Glycerol

DMHT Dimethylhexahydroterephthalate

DMT Dimethylterephthalate

TMAA Trimellitic Acid Anhydride

pTS p-toluene sulphonic acid

HMM Largely methyl-etherified commercial hexamethylol malamine (MAPRENAL MF 900 —MAPRENAL is a Registered Trade Mark)

MFC More highly reactive, partially methyl-etherified commercial melamine-formaldehyde condensation product; 90 percent solution in isopropanol (RESIMENE 730 —RESIMENE is a Registered Trade Mark)

Bl. Cat. Approximately 50 percent solution of a non-ionic blocked commercial acid (VESTURIT Catalysts BL 1203 — VESTURIT is a Registered Trade Mark)

AN Acid Number

H Pendulum hardness (DIN 53 157)

D Depression (DIN 53 156)

## WHAT WE CLAIM IS:—

1. A low-solvent or solvent-free liquid coating composition containing as binder

5 A) 45 to 10 percent by weight of an aminoplast resin and/or low molecular weight precursor(s) thereof 5

and

B) 55 to 90 percent by weight of an at least bifunctional polyester or polyester mixture bearing predominantly free hydroxyl end groups optionally together with carboxyl end groups,

10 the polyester(s) of Component B) being produced by condensing a component I, consisting of 10

I.1. 0 to 50 mole percent of one or more aliphatic polyols with 3 to 4 hydroxyl groups and 3 to 6 carbon atoms

and

15 I.2. 100 to 50 mole percent of a mixture II of aliphatic and cycloaliphatic diols, 15

the mixture II in turn consisting of

II.1. 10 to 90 percent of ethylene glycol and

II.2 90 to 0 mole percent of propane diol-(1,2)  
and

5 II.3. 0 to 40 mole percent of one or more other aliphatic or cycloaliphatic diols  
in which the hydroxyl functions are separated by 2 to 8 carbon atoms and  
up to 2 of the carbon atoms can be replaced by oxygen atoms which in turn  
are separated from each other and from the hydroxyl groups by at least  
2 carbon atoms, 5

with a component III, consisting of a mixture of

10 III.1. 67 to 92 mole percent hexahydroterephthalic acid  
and  
III.2. one or more aromatic dicarboxylic acids, 10

optionally followed by acidification to increase the acid number, the polyester or  
polyester mixture used as Component B) having a molecular weight of 300 to 1,500  
and the binder being optionally obtained by combined condensation of the aminoplast  
resin and/or low molecular weight precursor(s) thereof with the polyester(s) or by  
combined condensation of the basic material used to produce the aminoplast resin  
with the polyester(s), in which process terephthalic acid is used as Component III.2  
in an amount of from 8 to 33 mole percent based on component III. 15

2. A coating composition according to claim 1, wherein 12 to 25 mole percent  
(based on component III) of terephthalic acid units are present as Component III.2  
in the polyester(s) B. 20

3. A coating composition according to claim 1 or 2, wherein component I of the  
polyester(s) B) consists of 0 to 20 mole percent of glycerol or trimethylolpropane and  
100 to 80 mole percent of mixture II. 25

4. A coating composition according to any of claims 1 to 3, wherein mixture II  
for the polyester(s) B) contains from 10 to 90 mole percent of ethylene glycol, from  
10 to 90 mole percent of propane diol-(1,2) and from 0 to 30 mole percent of one  
or more other aliphatic or cycloaliphatic diols specified under II.3 in claim 1. 30

5. A coating composition according to any of claims 1 to 4 wherein the poly-  
ester(s) B) have an acid number of from more than 5 up to 20 mg KOH/g and have  
been obtained by reaction of polyester(s) B) having an acid number of less than  
5 mg KOH/g at from 130 to 190°C with a carboxylic acid or acid anhydride which  
is at least as acidic as maleic, phthalic, trimellitic or pyromellitic acid. 35

6. A coating composition according to any of claims 1 to 5, which also contains  
a pigment with or without a flow agent and/or a supplementary binder. 35

7. A coating composition according to claim 6, wherein the binder pigment ratio  
is from 1:0.3 to 1:1.3.

8. A coating composition according to claim 1 and substantially as described in  
any of the foregoing Examples. 40

9. A coating process in which a substrate is coated with a composition according  
to any of claims 1 to 8 and then stoved at from 100 to 250°C. 40

10. Articles which have been coated by a coating process as claimed in claim 9.

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